Effects of the Carnahan-Starling free energy within theories of fluids with short-range attraction

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Within the Free-Volume Asakura-Oosawa-Vrij (FVAO) theory of colloid-polymer mixtures, we show that unphysical gas-liquid binodals predicted in the regime of small attraction range (i.e. polymer size) are caused in part by the use of the Carnahan-Starling (CS) hard sphere (HS) reference free energy. Replacement of the CS expression with an alternative dramatically affects predicted phase behaviour and, for polydisperse colloid, the resultant fractionation predictions. Although short-range attractions render FVAO, as a perturbative HS-based theory, less accurate anyway, we argue that the particular effects of CS in this regime are an important consideration – usually ignored – in the evaluation of such theories. We refer to a variety of literature exhibiting similarly inaccurate gas-liquid binodals, and suggest CS's status as the *de facto* choice of hard sphere reference should be carefully considered where short-range attractions are present.

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I. INTRODUCTION

Long ago, Widom [1] explained why excluded-volume, or equivalently entropic, effects should dominate the behaviour of liquids around the triple point. The long-range inter-particle attractions (e.g. as modelled by a van der Waals potential) of $\gtrsim 10$ nearest neighbours sum approximately to a constant. To a first approximation, therefore, the inter-particle attraction simply lowers the internal energy component of the Helmholtz free energy by a fixed amount. Minimising the free energy is then equivalent to maximising the entropy. This qualitative argument underpins the success of the use of repulsive particles in general [2], and hard spheres in particular [3], as reference systems in perturbation theories of the liquid state.

In the hard sphere (HS) model, particles interact via a step-like repulsive potential which is infinite at contact and zero everywhere else:

$$V_{\mathrm{HS}}(r) = \begin{cases} \infty & \text{if } r \leq d \\ 0 & \text{if } r > d \end{cases} \tag{1}$$

where $d = 2a$ is the HS diameter and r the distance between particle centres. This model has a long history in the study of fundamental statistical mechanical problems of the condensed state. Thus, e.g., there was the celebrated question of whether a collection of hard spheres would crystallise at high enough number density [4], which was eventually settled in the affirmative first using computer simulations [5], and then more recently using experiments on colloids in which the particles interact as nearly-perfect hard spheres [6]. These latter experiments took hard spheres into the laboratory. They have now been used to study everything from the kinetics of crystal nucleation [7] to the glass transition [8]. In such experiments, very direct confrontation with analytic calculations and simulations is possible – there is in principle only a single, experimentally accessible, parameter - volume fraction [9], which for N hard spheres of diameter d filling a volume V is $\phi = \pi N d^3/6V$.

Inter-particle attraction can be induced in colloids by adding non-adsorbing polymers: exclusion of polymer molecules from the region of space between the surfaces of two nearby particles results in a net osmotic force pushing the particles together. The range of this 'depletion' attraction is controlled by the size of the polymer, e.g. as measured by its radius of gyration r_g. The strength of the depletion attraction is proportional to the polymer's chemical potential, or, equivalently, the number density n_R of polymers in a reservoir in osmotic equilibrium with the colloid-polymer mixture. A well-characterised colloid-polymer (CP) mixture of this kind, hard-sphere-like sterically-stabilised particles of poly-methylmethacrylate (radius a) and the non-adsorbing polymer polystyrene, has been used to study a range of basic condensed matter questions (reviewed in Ref. [10]). In particular, experiments using this system have demonstrated that a gas-liquid coexistence region only exists in the equilibrium phase diagram when the depletion attraction is of long enough range: $r_g/a \gtrsim 0.24$.

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A simple model of the depletion attraction, the Asakura-Oosawa-Vrij (AO) model [11, 12], treats the colloids as hard spheres, of radius a; the polymers are (smaller) spheres, of radius $\delta \approx r_g$ that interpenetrate one another, but have a hard sphere interaction with the colloids. The AO model has been incorporated into a free-volume theory for calculating the phase behaviour of CP mixtures [13]. This Free-Volume AO (FVAO) theory requires as input reference free energies of hard spheres in the fluid and crystalline states. For the latter, a parameterised expression from simulations [14] is available. For the HS fluid, a simple closed form expression given by Carnahan and Starling (CS) [15] is the default choice [13, 16–18].

The CS free energy is obtained from integrating the CS equation of state (EOS), which is usually given in terms of the compressibility factor, $Z = PV/mk_BT$ relating the pressure P, volume V and temperature T of m moles of hard spheres:

$$Z_{\rm CS} = \frac{1+\phi+\phi^2-\phi^3}{1-\phi^3}\ . \tag{2}$$

This is known to represent simulation data accurately, at least at low to moderate ϕ, but is self evidently unphysical at high ϕ, since it does not diverge until $\phi = 1$, whereas a monodisperse hard sphere fluid may only be packed to random close packing, $\phi_{\rm RCP} \approx 0.64$, and even the ordered (crystalline) close packing value is only $\phi_{\rm close} = \pi/3\sqrt{2} \approx 0.74$. While there is by no means consensus as to the "correct" behaviour of the hard sphere equation of state at high ϕ [19] (especially given that, very close to $\phi_{\rm RCP}$, jamming and path-dependent effects come into play [20]), it is clear that CS's high ϕ behaviour cannot be accurate. This unphysical feature of the CS EOS matters little in many contexts. However, we argue in this note that it contributes to unphysical predictions of phase behaviour in the FVAO theory of CP mixtures in the regime of small size ratios, $q = \delta/a \ll 1$. On replacing the CS EOS with one that is more realistic at high ϕ, we find a marked change in the predicted phase behaviour at small q. This leads also to important consequences when the colloid in a CP mixture is polydisperse: the fractionation upon phase separation predicted by the two approaches differ by an order of magnitude.

Unphysical gas-liquid binodal predictions in FVAO and those in similar theories [18] are usually attributed to the increasing unsuitability of HS-based perturbative theories as attractions become shorter-ranged: correlations become less HS-like, and the HS reference itself becomes significantly metastable. We stress from the outset that this remains the case no matter what choice of HS reference is used – modifying FVAO by replacing CS still results in poor comparisons with available simulation data, and recent work improving on e.g. the approximation of non-interacting polymers [21] remains necessary and well-motivated. However, we argue that the tendency of shorter-range attractions to bring particles closer together necessarily renders the high ϕ behaviour of a HS reference more important, in a variety of theories, so that testing specifically for dependence on CS is an important step in evaluating their predictions.

II. THE FVAO THEORY

A. Free energy and hard sphere compressibility factor

In treatments of CP mixture phase behaviour prior to the FVAO theory, the AO depletion potential (which, for $q < 0.154$, maps exactly to an effective pair potential [18]) was used as a perturbation to the HS reference. In FVAO, the free energy contribution of the (ideal) polymers is obtained directly, explicitly allowing for partitioning of polymers between the phases. Within FVAO [13], the Helmholtz free energy per unit volume of the mixture is found to be the sum of two terms (with $k_BT \equiv 1$):

$$f = \frac{3}{4\pi a^3}\phi \int \frac{Z_{\rm HS}}{\phi}\, d\phi + n \ln n_R \tag{3}$$

where $Z_{\rm HS}(\phi)$ is the HS compressibility factor, a the colloid radius, n the polymer number density and n_R the polymer number density in a reservoir in osmotic equilibrium with the CP mixture (i.e. coupled to the system via a membrane through which only polymer and solvent may pass). Note that the apparent separation in colloid and polymer terms in this expression is deceptive, since n_R is related to the concentration of polymers in the volume left accessible to them by the colloids: $n_R = n/\alpha$ where $\alpha(\phi)$ is the free volume fraction left by the colloids. We follow the original FVAO prescription [13] that α takes the same value as at zero polymer fugacity and is given by a scaled-particle (or equivalently, Percus-Yevick) [22] result. We note that this assumption – which renders FVAO, too, an essentially perturbative theory – becomes less appropriate as attraction range decreases [18], but it is sufficient for our purpose of comparing an approximate treatment involving CS to another choice of reference.

To apply Eq. 3, fluid and crystal branches of $Z_{\rm HS}$ are required, with integration constants chosen to reproduce the known fluid-crystal coexistence gap in the HS phase diagram. Since we only deal with gas-liquid coexistence in this work, integration constants are not required.

In the original implementation of the FVAO theory and most subsequent applications, $Z_{\rm HS} = Z_{\rm CS}$, Eq. 2, is used as the fluid compressibility factor in Eq. 3. We compare $Z_{\rm CS}$ with an alternative approximate form, the 'WKV3' expression originally given in Ref. [23]. It is given by:

$$Z_{\rm WKV3} = \frac{1}{\xi}\sum_{i=1}^{7} D_i \left(\frac{\xi}{1-\xi}\right)^i , \tag{4}$$

where $\{D_i\}$ denote a set of seven coefficients, and $\xi = \phi/\phi_{\rm close}$ [23]. Note that this expression does not diverge

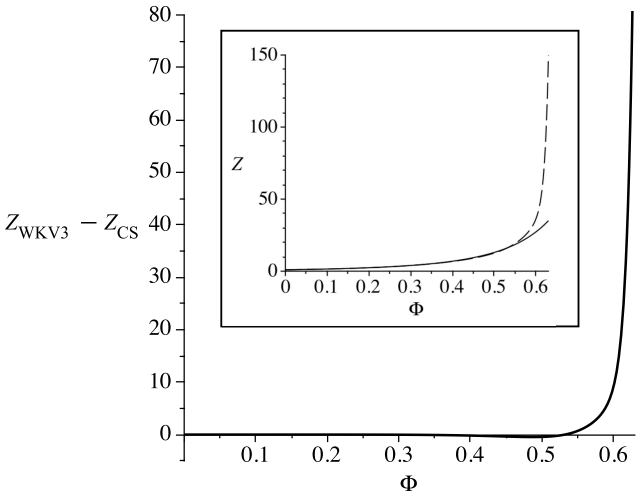

FIG. 1. The difference, $Z_{\mathrm{WKV3}} - Z_{\mathrm{CS}}$, between the two HS fluid compressibilities considered, as a function of volume fraction. Inset: behaviour of Z_{WKV3} (dashed) and Z_{CS} (full line).

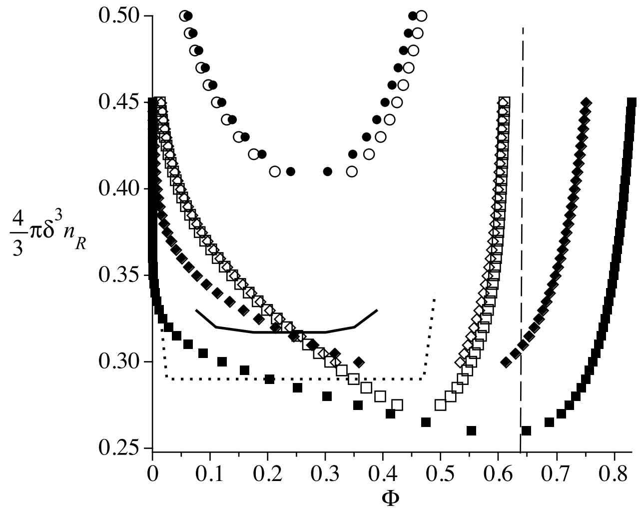

FIG. 2. FVAO gas-liquid binodals calculated with two choices of Z_{HS}, Eqs. 2 and 4. The filled symbols show Z_{CS}, the open ones Z_{WKV3} for $q = \delta/a = 0.4(\circ, \bullet), 0.15(\lozenge, \blacklozenge), 0.1(\square, \blacksquare)$. Dashed line: $\phi = 0.64 \approx \phi_{\mathrm{RCP}}$. For comparison, the solid line shows the simulated binodal for $q = 0.15$ from Ref. [30], and the dotted line that for $q = 0.1$ from Ref. [18]. At $q = 0.1$, recent simulations [34] find a critical colloid packing fraction $\phi = 0.249$. However, the position of the critical point (where mean-field theories are unsuitable) is not the focus of the present work, rather the position of the liquid binodal at higher n_{R}.

at ϕ_{RCP}, as might be expected for a HS fluid, but rather at ϕ_{close}. A recent review [19] recommends Z_{WKV3} as the best expression for the HS fluid at high ϕ, but the difficulty of simulating in this region to determine what constitutes "best" qualifies such a recommendation. In the present context, the important feature of WKV3 is that it closely matches CS at low to moderate ϕ, but differs on approaching ϕ_{RCP} and above. This difference should become more important as attraction range decreases, so WKV3 serves as a good choice to illustrate the sensitivity of predictions to the choice of HS reference. Fig. 1 shows that Z_{CS} and Z_{WKV3} are nearly identical for $\phi \lesssim 0.55$, but Z_{WKV3} overtakes Z_{CS} beyond that point, with the difference becoming increasingly marked as $\phi \to \phi_{\mathrm{RCP}}$. We now turn to explore the consequences of this difference for phase behaviour at small q.

B. Phase behaviour

A full implementation of the FVAO theory encompassing fluid and crystal phases shows that gas-liquid coexistence with monodisperse colloid is thermodynamically stable only when $q \gtrsim 0.3$. At low q, therefore, the unphysical divergence of Z_{CS} as $\phi \to 1$ has little effect on the equilibrium phase diagram, since the density of the crystal phase is determined largely by the behaviour of the Hall expression [14] near $\phi_{\mathrm{close}} \approx 0.74$. However, the *metastable* gas-liquid binodal remains important, since it plays a key role in phase transition kinetics [24–33], e.g. enhancing crystal nucleation [25, 30], splitting advancing crystal interfaces [31, 32], or causing nonequilibrium behaviour such as gelation [33]. Here we therefore neglect the crystal branch of the free energy and consider the gas-liquid binodals predicted by Eq. 3 with Z_{CS} and Z_{WKV3}.

By equating relevant derivatives of Eq. 3, which give the pressures and chemical potentials in coexisting phases, we calculate the gas-liquid coexistence boundaries (or binodals) at different q [13] with Z_{HS} given by Eqs. 2 and 4, Fig. 2. Note that the vertical axis here gives the polymer reservoir concentration, which is directly related to the polymer chemical potential, so that tie lines in this representation are horizontal.

At the moderate size ratio of $q = \delta/a = 0.4$, the two choices of Z_{HS} give similar results. However, when q is reduced, utilising Z_{CS} results in the liquid side of the binodals exceeding ϕ_{RCP}, i.e. the maximum possible volume fraction of a HS fluid, which is unphysical. At $q = 0.1$, even the maximum crystalline packing, $\phi_{\mathrm{close}} \approx 0.74$, is exceeded. This is because when Z_{HS} is used to calculate coexistence, the liquid does not pay a high enough free energy penalty for approaching and then exceeding unphysical concentrations. In contrast, in the same range of q, utilising Z_{WKV3} results in binodals whose liquid sides stay below ϕ_{RCP}.

Fig. 2 includes simulated gas-liquid binodals at low-q from Refs. [18, 30], which still compare poorly with FVAO when WKV3 is used (note also that the $q = 0.1$ critical colloid packing fraction $\phi = 0.249$ found in recent simulations [34] is approximately a factor of 2 lower than the apparent location using FVAO and WKV3). As discussed in the Introduction and extensively in Ref. [18] FVAO, as a perturbative theory assuming zero polymer

fugacity, remains inaccurate at low-q for reasons additional to the use of CS.

Given this, it is important to emphasise that our aim is to illustrate the *sensitivity* to choice of HS reference brought about by short-range attractions, and not to imply that all inaccuracies in this regime are due solely to the use of CS. FVAO simply serves as a well-known archetype of a wide class of theories which build upon the hard sphere reference.

We note that unphysically high liquid densities have also been found in the gas-liquid binodals predicted by more sophisticated models of CP mixtures at low q (e.g. [21]) as well as liquid-state theories of other systems with short-range attraction (e.g. [17, 18, 21, 35–39]). In each case cited, the CS reference free energy is used exclusively and without question. In addition to other dangers that can affect *any* HS reference in this regime [18], we suggest that CS is a specific, important factor whose influence on predicted gas-liquid binodals should be tested in the course of evaluating predictions at short attraction range. Motivating this is the generic observation that shorter-range attractions, however they are incorporated into a theory, should act to compress the liquid phase, favouring the minimisation of interaction energy – broadly speaking, the role of the hard sphere reference is to define the penalty the system pays for this compression which, for CS, becomes spuriously low at higher ϕ. Thus, as attraction range is decreased within perturbative (and perhaps even non-perturbative [17]) theories, it becomes more important to test for dependence on CS in order to distinguish its effects from those intrinsic to the theory in question.

Concluding this section, we note that for the purpose of precisely predicting a critical point, it appears sufficient and preferable to use a criterion based on the second virial coefficient B_2 [34, 40], which gives good agreement down to low-q and avoids the concerns outlined above. However, the behaviour of binodals away from the critical point cannot be discerned by these means, and this behaviour is important e.g. for determining the relationship between binodals and features such as gelation or vitrification lines [17], predicting crystal growth kinetics [24, 29], and predicting fractionation between separating phases [41, 42]. In respect of the latter, we now turn to illustrate the effects of the choice of $Z_{\rm HS}$ on fractionation predictions in the case of polydisperse colloid, where the metastable gas-liquid binodal is particularly important since crystallisation is suppressed in experimental realisations.

III. POLYDISPERSITY AND FRACTIONATION

When inter-particle attraction causes a gas-liquid type transition in a colloidal suspension in which the particle size distribution has finite polydispersity (defined as the standard deviation divided by the mean of the size distribution), the two daughter phases not only differ in their particle number densities, but also in their size distributions.

We distinguish between two well-known formulations: a perturbative approach [43], and a moment free energy approach [44–46]. In the former, only a free energy for the *monodisperse* (single-sized) reference system is required, whereas the latter requires a polydisperse model free energy, such as the Boublík-Mansoori-Carnahan-Starling-Leland (BMCSL) one [47], which generalises CS. In the context of CP mixtures, both can be applied to the FVAO theory [43, 45]. Since the perturbative approach allows substitution of the (monodisperse) $Z_{\rm WKV3}$ into the existing theory, we examine fractionation in this context. However, as the BMCSL free energy inherits the $\phi = 1$ divergence of the parent CS expression, we expect the findings to be also of relevance to the moment free energy approach. Indeed, our findings are likely generic to *any* treatment of fractionation in which some form of approximate HS-like free energy is used.

In the perturbative treatment [43], the fractionation, or difference in mean particle diameter ($\langle\epsilon\rangle$) between coexisting gas (g) and liquid (l) phases, is given by:

$$[\langle\epsilon\rangle]_g^l = -[A/\rho]_g^l \sigma_p^2, \tag{5}$$

where $A(\rho) = \rho[\partial\mu^{\rm ex}(\epsilon)/\partial\epsilon]$ describes, in a monodisperse reference system, the variation in excess chemical potential $\mu^{\rm ex}$ as a function of fractional size deviation ϵ (positive or negative) from the overall mean diameter. It is the rate of change of excess chemical potential with particle size. The variance of the parent distribution is σ_p^2. Thus, $-[A/\rho]_g^l$ controls the 'fractionation strength' – it gives the fractional difference in mean diameter between phases, normalised by the overall variance. For a CP mixture, plotting $-[A/\rho]_g^l$ as a function of polymer reservoir volume fraction is therefore a convenient way of seeing how much fractionation results at various strengths of the depletion attraction (see [43] for details). We show such a plot at different size ratios, $q = \delta/a$ in Fig. 3 calculated within the perturbative framework [43] using $Z_{\rm CS}$ and $Z_{\rm WKV3}$.

As in the case of the binodals, Fig. 2, there is little difference at $q = 0.4$; but the two compressibility factors give progressively more divergent predictions for the strength of fractionation as q decreases. In the case of the binodal, the unphysical nature of the predictions made using $Z_{\rm CS}$ is immediately obvious on physical grounds: a liquid cannot pack at $\phi > \phi_{\rm RCP}$. No such intuition guides our evaluation of the predictions presented in Fig. 3 because to date, there are relatively few detailed experimental, theoretical or simulation studies of fractionation.

Some precise results are emerging for pure HS systems (e.g. [48–50]). For CP mixtures, experiments [51–53] have tested and confirmed the scaling of fractionation strength with parental variance embodied in Eq. 5. However, in these experiments, $-[A/\rho]_g^l$ is a fixed constant that need not be actually known. They therefore do not test the accuracy of any theoretical predictions for $-[A/\rho]_g^l$, i.e. the absolute degree of fractionation at

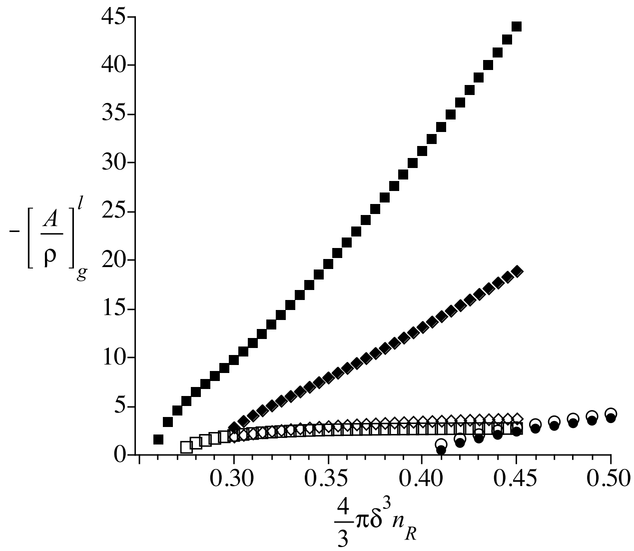

FIG. 3. Predicted fractionation strength as a function of polymer reservoir volume fraction in a CP mixture with polydisperse colloids, within Evans's perturbative theory applied to the FVAO theory, with two choices of the HS compressibility factor. The filled symbols show Z_{CS}, the open ones Z_{WKV3} for $q = \delta/a = 0.4(\circ, \bullet), 0.15(\diamondsuit, \blacklozenge), 0.1(\square, \blacksquare)$.

a given parental variance. Later, predictions made using the moment free energy method [45] showed reasonable quantitative agreement with the aforementioned experiments in terms of *both* the absolute degree of fractionation as well as its scaling with the parent distribution width; however, these were only performed at moderate size ratio, where the poor performance of CS has little impact. A combined experiment, theory and simulation study based on recently published data [41] that is aimed at testing calculated values of $-[A/\rho]_g^l$ for a CP mixture at low q is under way. However, Fig. 3 already serves to illustrate that the behaviour of Z_{CS} for short attractions has significant consequences not just for the overall phase behaviour but, perhaps more so, for supervening theories such as the perturbative theory of polydispersity tested here.

IV. CONCLUSIONS

In this paper, we have studied the FVAO theory of CP mixtures as a representative HS reference-based theory, in the regime where the polymer to colloid size ratio, $q = \delta/a \approx r_g/a$, is significantly less than unity, so that depletion attraction induced by the polymers between the colloids is short-ranged. By testing an alternative expression for the HS compressibility factor, Z_{WKV3}, we showed that the known unphysical behaviour of the gas-liquid binodal in this regime could be attributed in part to the use of the Carnahan-Starling hard sphere free energy, whose divergence at $\phi = 1$ allows the liquid to be compressed more than is physically possible at a spuriously low free energy cost; although CS-independent failings of FVAO at low-q remain very important. Many other expressions for Z_{HS}, and details of their accuracy, are available [19]. We chose one of these, WKV3, for its similarity to CS at moderate ϕ and strong difference at higher ϕ [19], using it as an alternative input to the FVAO theory to demonstrate the *sensitivity* of predictions in the short attraction range regime to the choice of Z_{HS}, and so the importance of this choice in making and evaluating such predictions. In particular, we showed that at $q \lesssim 0.2$, the use of Z_{CS} and Z_{WKV3} lead to quite different results both for the gas-liquid binodal and for the degree of fractionation when the system is polydisperse.

In a wide variety of theories (in which CS is the *de facto* choice for Z_{HS}) [17, 18, 21, 35–39], predicted gas-liquid binodals are found to become increasingly inaccurate as attraction range decreases; it seems likely that CS constitutes a specific common point of failure, *in addition* to the general difficulty in deploying a HS reference in this regime. We emphasise that in none of these examples is the unphysical divergence of CS noted, nor is any other choice of Z_{HS} entertained. This could be particularly important in studies such as that reported in Ref. [17], where the CS reference is used alongside a Yukawa potential, a crystal phase, and a mode coupling theory. In such situations, a significant quantitative change in position of the gas-liquid binodal could then qualitatively alter its relationship to those other elements of the phase diagram. Similarly, it could be important in interpreting findings (e.g. [36]) in which multiple independent theories disagreeing with simulation are in fact all *dependent* on the same CS free energy.

Predictions of phase behaviour and related phenomena (e.g. fractionation) in systems with short-range attractions can easily be tested for dependence on Z_{CS} by a similar procedure to that performed here. Otherwise, detailed analysis of a theory's performance may be ill-founded, given that large discrepancies caused by using the CS expression (separate to those intrinsic to the theory incorporating it) may go unnoticed and unquantified.

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